Comparison of Different Types of Carbamate Amine for Stripping Process

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Amine absorption process is an approach for mitigation of carbon dioxide (CO_2) from flue gas that was produced from the power plant. Modelling and simulation of amine absorption process for CO_2 removal at macro-scale is well established. This study aims to investigate different carbamate molecules for the regeneration process using molecular dynamic (MD) simulation. MD simulation was installed in the HP240 workstation using the software of Material Studio (version 7.0). The MD simulation was carried out at mole, volume, energy (NVE) (200 ps) and mole, volume, temperature (NVT) (1 ns) ensemble. Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) and Ewald models were used for the force field and summation method calculation within the simulation box. The simulation results show that, the carbamate ions of monoethanolamine (MEA) were difficult to break compared to 2-amino-2-methyl-1-propanol (AMP) and piperazine (PZ) for inter- and intra-molecular interactions on the stripping process. The high tendency for inter- and intra-molecular interactions happened on AMP and PZ, making them good choices to be blended with other amine solvent to overcome the limitation of other less reactive amines. The simulation results obtained from this study gave the fundamental explanation on the experimental and simulations results reported in the literature. The application of MD simulation in amine absorption process is capable to improve the understanding and give insight about this process at molecular level.

1. Introduction

Due to the increased carbon dioxide (CO_2) composition in the atmosphere and its effect to global warming, researchers, academicians and industrialists are concern to discover the method for capturing CO2 acid gases. Another effect from the CO_2 emission are health problems, acid rain and urban smog. CO_2 emission happened from the burning of fossil fuels. The average annual concentration of CO_2 has increased 2.1 part per million (ppm) per year from 2005 to 2014 (ProOxygen, 2016). There are many methods available in carbon capture and sequestration (CCS) technologies that can be used to capture CO_2 from existing emission source and prevent the emission to ozone (Raganati et al., 2015). In this study, chemical absorption process is considered to capture CO_2 using one of the established absorbents, namely the alkanolamines (Kohl and Nielsen, 1997).

There are many published research studies reported on the amine-based absorption process using the computational method. Farmahini (2010) studied about the blended Piperazine/Methyl-diethanolamine (PZ/MDEA) absorption proses for Methane (CH_4) and CO_2 using Molecular Dynamic (MD) simulation. From this dissertation, it shows that small amount of PZ can accelerate the CO_2 absorption process by MDEA solvent. The following year, Farmahini et al. (2011) reported that the MDEA blended with PZ offered a good combination for CO_2 absorption process. The PZ molecule forms protonated piperazine (PZH+) and piperazine carbamate (PZCOO-) that cause high solubility in water. Formation of PZCOO- accelerated the absorption process. Maiti et al. (2010) conducted the atomistic modelling for CO_2 capture using primary and tertiary amines. Their research applied Quantum chemical and classical MD simulation. The speciation was evaluated based on the fraction of ionic species, density and volume changes and ionic association. The solvation shell of carbamate ion in monoethanolamine (MEA) was bigger compared to bicarbonate ion in MDEA. They showed that MEA was able to absorb more CO_2 than MDEA. Similar approach was used by

Singh (2011) but using the solvent hexamethylenediamine (HMDA) for CO_2 absorption process. The absorption rate decreased with the increase in chain length of amine. Singh (2011) performed the modelling studied of CO_2 absorption using alkanolamine solutions. Their simulation work used the Density Functional Theory (DFT) with dielectric continuum solvation models and Conductor-like Screening Model for Realistic Solvents (COSMO-RS) model. They found that the alcohol chain length of alkanolamine affected the yield of CO_2 absorption process. Matsuzaki et al. (2013) applied the Polarizable Continuum Model (PCM) and Ab Initio Molecular Orbital method to study the inter-conversion of carbamate and bicarbonate for MEA. They proposed a new pathway mechanism, where the proton ion was transferred from carbamate to form bicarbonate ion and MEA. Emmanuelle (2013) shows that MEA has high CO_2 diffusivity compared to MDEA and ethylamine due to small spatial configuration and low amount of hydroxyl group in the amine structure. Sumon et al. (2014) studied the reaction mechanism involved in CO_2 absorption process using Ab Initio in MD simulations. The structures for carbamate zwitterions (R1R2NHCOO±) and carbamic acid (R1R2NCOOH) were observed. Hwang et al. (2015) also studied the chemical reaction mechanism. From the quantum chemical calculation, a zwitterion-mediated two-step mechanism was used in the reaction of amine with CO_2 absorption and regeneration process. Kachko et al. (2016) used the Aspen Plus model with chemometrics approach for the simulation of CO_2 absorption by aqueous MDEA. Solutions activated by PZ were used for the properties estimation of the liquid solvent under pilot plant conditions. Prakash and Venkatnathan (2016) studied the CO_2 absorption process using ionic liquid (IL). The CO_2 was absorbed in the bulk IL layers during the first 10 ns. The action of CO_2 was more on the cations of the IL compared to the anions.

Most of the previous research work has focused on the computational chemistry, notably regarding the calculation of ionic and enthalpy effect for the CO_2 absorption process. This study aims to apply the computational chemistry studies focusing on the physical inter- and intra-molecular interaction in the CO_2 regeneration process. There is research gap for the physical molecular interaction in the open literature for CO_2 regeneration process. Molecular dynamic (MD) simulation is one of the powerful computation modelling tools used to calculate the mass transfer properties such as diffusivity (Wang and Hou, 2011). This simulation can be used to study the behaviour of complex system for model at atomic level. All molecular structure simulated in the MD simulation are replicated from the actual macroscopic system. Most calculation conducted by MD simulation is difficult to be carried out by the laboratory experimental. The MD simulation is performed to speed up the calculation, provide visualized image for the reaction of the absorption process in environmental friendly and economical saving manners (Charpentier, 2002). Changes of molecule structure through time evaluation in simulation can be seen to give deep understanding about the chemical reaction for CO_2 absorption. The computational technique is useful to proof the hypothesis parameter prior to the laboratory experiments (Farmahini, 2010). Radial distribution function (RDF) analysis will be conducted using the MD simulation to analyse the physical inter- and intra-molecular interaction. RDF analyses are applicable to define the behaviour of gas, liquid, solid phase and the mixtures. It can also calculate the thermodynamic functions of the spherically symmetric molecules $g(r,\rho,T)$ (Bamdad et al., 2006). The graph from the RDF analysis shows the correlation between r, the distance between atom pairs in each of the trajectory with the neighbouring atom and g(r), the probability interaction of atom interact with other atom.

One of the challenges in amine absorption process is the high energy requirement for stripping process to remove the CO_2 from the carbamate ion and the amount of absorbing capacity must be over several absorption process cycle (Miccio et al., 2015). The stripping process in the regeneration column occurred at high temperature where the mixture of amine and CO_2 acid gas was separated at this stage. MEA, AMP, and PZ carbamate amines were used in this study to analyse the stability of carbamate ions for separating CO_2 from the amine solution. This study is aims to compare the simulation result of the inter- and intra-molecular reaction of amine carbamate with water which represent the tendency of carbamate to break the bond and release CO_2.

2. Simulation Method

The simulation was performed using Material Studio (7.0) software on HP Z400 workstation supplied by Accelrys (2014). There are six main steps in the simulation, i.e. sketch the molecular structure, construct the simulation box, minimize the energy in the simulation box, run the dynamic simulation and conduct the analysis for Inter- and intra-molecular interaction. The molecular structure was download from established database (Chemspider, 2016). The amorphous cell box was constructed to represent the bulk system. The size of the box was depended on the amount of molecule inserted. The energy within the box have to minimize before proceeding to the dynamic simulation which represents the equilibrium and production step. Two hundred ps NVE (moles, volume, energy) and one ns NVT (moles, volume, temperature) were used for each step. The parameter set in this simulation was the atom based summation method (for geometry optimization), Ewald summation method (for equilibrium and production phase), COMPASS force field (for

energy interatomic potential calculation), and velocity Verlet algorithm (for time integrator algorithm calculation). The final structure on the production step was used for the analysis purpose. Radial Distribution Function (RDF) calculation was carried out to analyse the inter- and intra-molecular interaction between the molecules in the simulation box. In this study, a few types of amine used were methyl carbamate (MEACOO-), 2-amino-2-methyl-1-propanol carbamate (AMPCOO-), piperazine carbamate (PZCOO-). Their molecular structures are shown in Figure 1. All carbamate amines are analysed at 30 wt. %, 313 K and 1 atm.
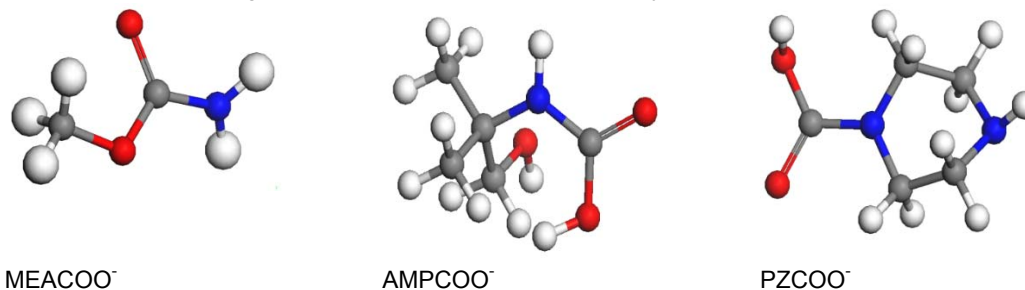

MEACOO⁻   AMPCOO⁻   PZCOO⁻

Figure 1: The molecular structure of Methyl carbamate (MEACOO⁻), 2-amino-2-methyl-1-propanol carbamate (AMPCOO⁻), Piperazine carbamate (PZCOO⁻)

The radial distribution function (RDF) calculation is calculated from the trajectory file as per Eq. (1).

$$g_{xy}(r) = \frac{< N_y(r, r + dr)}{\rho_y 4\pi r^2 dr}$$

(1)

where $N_y(r, r+ dr)$ is the number of y atom in the shell of width *r* at distance r, r is the spherical radius, ρ_y is the density of y atom and x is the reference atom.

3. Results and Discussion

The stripping process is the most costly section in the absorption process due to high temperature required to break a bond between amine-CO_2. The stripping process is also known as the regeneration process. Regeneration is a process to remove the acid gases from the rich solvent phase after the absorption process. The simulation was run based on the intermolecular interactions between MEACOO⁻, AMPCOO⁻, or PZCOO⁻ with the water to observe the tendency of CO_2 to react with water to form the bicarbonate ions that represent the attraction force. The intramolecular interactions between $N_{carbamate}$ and $C_{carbamate}$ in MEA, AMP, and PZ which represent the repulsion force was also studied. The RDF analysis shows how the inter- or intra-molecular interactions have taken place between the atoms or molecules.

3.1 Intermolecular interaction between carbamate amine and water

The intermolecular interaction between three types of carbamate amines, i.e. the conventional amine, MEA, the activator amine, AMP and PZ, were simulated to identify which amine solvent has a strong intermolecular interaction (attractive interaction) with water. The simulation results are presented in Table 1 where *r* and *g(r)* represent the distance of atom with other neighbour atom and probability for interaction to occur.

Table 1: RDF results for the attractive interaction between carbamate amine with water

	MEA (*r, g(r)*)	AMP (*r, g(r)*)	PZ (*r, g(r)*)
$C_{carbamate}$-O_{water}	3.75, 1.1398	3.75, 1.3833	3.75, 1.1309
$N_{carbamate}$-H_{water}	3.75, 1.0068	5.75, 1.1036	5.25, 1.0593

$C_{carbamate}$: Carbon atom in the carbamate molecule; $N_{carbamate}$: Nitrogen atom in the carbamate molecule
O_{water}: Oxygen atom in water; H_{water}: Hydrogen atom in water

Table 1 shows the RDF results for the attractive interaction between the carbamate ions, MEA, AMP, and PZ with water. As shown in Table 1, $C_{carbamate}$-O_{water} has high peak attractive interaction compared to $N_{carbamate}$-H_{water} refer to value *g(r)*. For example, MEACOO⁻ has the first peak at 3.75 Å with a value of 1.1398 implying that there was almost 13.21 % tendency to find the pair of atoms to make interaction for $C_{carbamate}$-O_{water} compared to 1.0068 for $N_{carbamate}$-H_{water}. For the AMP molecule, $C_{carbamate}$-O_{water} has a short distance to make the first peak interaction within 3.75 Å, while $N_{carbamate}$-H_{water} has interaction at a distance of 5.75 Å. The attractive interaction between $C_{carbamate}$-O_{water} was also higher because the carbamate ions tended to react with water to form the bicarbonate and recycled amine. This interaction is also known as the ion dipole

bonding. The interaction between $N_{carbamate}$-H_{water} was lower because it only formed the hydrogen bonding. It is in agreement with the fact as the ion dipole bonding is stronger than the hydrogen bonding. According to Hunt et al. (2015), the hydrogen bonding only involve the partial charges of the molecules while the ion dipole bonding involves a full charged ion and partial charge of the dipole molecule. In the hydrogen bond have ionic and covalent bond. The movement of charge from ion dipole bonding will forming a hydrogen bond. On the other hand, the water molecule is not linear and the centre of the positive charges does not coincide with the centre of the negative charges. Hence, it is a polar molecule (a dipole) that makes the carbamate ion tends to form the ion dipole bonding with water. Figure 2 illustrates the mechanism for the attractive interaction between the carbamate ions and water in MEA solvent to separate the CO_2 molecules from the amine compound.
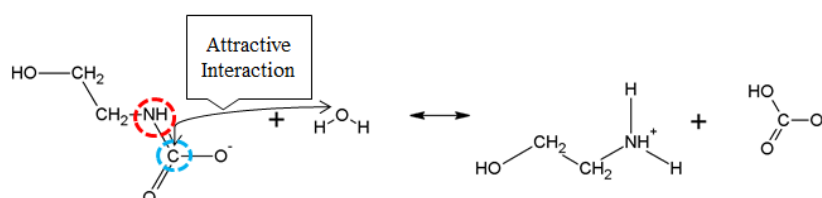

Figure 2: Example mechanism for the attractive interaction between the carbamate ions with water in MEA solvent. $N_{carbamate}$ and $C_{carbamate}$ are in red and blue circle.

Comparing the interaction between the MEA, AMP, and PZ and water ($C_{carbamate}$-O_{water}) shows that AMP has the highest attractive interaction with water. At a distance of 3.75 Å, the chances of finding pair of atoms were 1.3833, 1.1398, and 1.1309 for AMP, MEA, and PZ. It shows a 22.32 % chances of interaction by AMP compared to PZ. It is expected due to the steric hindrance properties of AMP that affect the carbamate stability of AMP.

In contrary, comparison between MEA, AMP and PZ with water ($N_{carbamate}$-O_{water}) shows that MEA has the highest attractive interaction with water. Within a short distance ($r = 3.75$ Å), there is a peak of interaction compared to others at 5 Å and above. The values of r and $g(r)$ for MEACOO⁻, AMPCOO⁻, and PZCOO⁻ were (3.75, 1.0068), (5.75, 1.1036) and (5.25, 1.0593). Based on the RDF results, water has higher tendencies to make attractive interaction with MEA.

3.2 Intramolecular interaction between $C_{carbamate}$ and $N_{carbamate}$

The strength of the intramolecular interaction (repulsive interaction) between $C_{carbamate}$ and $N_{carbamate}$ is discussed in this subsection. The intramolecular interaction (repulsive interaction) of $N_{carbamate}$-$C_{carbamate}$ was found as the main interaction due to the high-energy requirement to break the bond of the carbamate ions during the stripping process. Table 2 shows the RDF results for the repulsive interaction between carbamate ions and CO_2 where r and $g(r)$ represent the distance of atom with other neighbour atom and probability for interaction to occur.

Table 2: The RDF results for the repulsive interaction between C-carbamate and N-carbamate

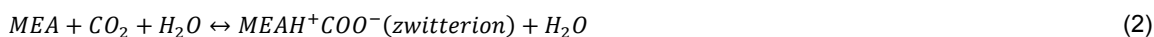|	$N_{carbamate}$-$C_{carbamate}$ (r, $g(r)$)
MEA	1.25, 20.0273
AMP	1.25, 36.5978
PZ	1.25, 42.6252

$N_{carbamate}$: Nitrogen atom in carbamate molecule
$C_{carbamate}$: Carbon atom in carbamate molecule
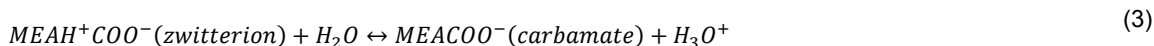
Table 2 shows the repulsive interaction between the three amines (MEA, AMP, PZ) and COO⁻. PZ has the strongest repulsive interaction compared to MEA and AMP. PZ shows about 212.84 % strength of repulsive interaction compared to MEA. This is because PZ forms bicarbonate ions and breaking of the C−O bonds requires less energy in the bicarbonate and carbonate breakdown than that required for breaking C−N bonds in the breakdown of carbamate (Kim et al., 2011). The application of PZ and AMP in the amine-based absorption process is a better choice. The tendency to interact with water to form the protonated amine and breaking the bond within the covalent bond of N-C were higher compared to the primary amine, MEA. When there was a high tendency for repulsive interaction, it required a minimum heat to break the bond. The application of AMP and PZ can lower the heat duty for the regeneration of amine solvent in the CO_2 capture process (Zhang et al., 2016).

With reference to the repulsive interaction in MEA, carbamate ions of high stability were produced that caused difficulty in breaking the bond. It is was reported that MEA was good in absorption but showed limitation in the stripping process (Damartzis et al., 2015). According to Damartzis et al. (2015), MEA have advantage with high reactivity with CO_2 while the disadvantage is required high heat demand for regeneration process. The heat duty of solvent regeneration is controlled mainly from the reactions as described in Eqs. (2), (3), and (4) because these reactions are highly endothermic, which according to (Caplow, 1968). Hydrogen ion was used to catalyze the decarboxylation of carbamate. In a rapid equilibrium, proton transfer happen from water. The extend study has been studied by (Shi et al., 2014), where there are an endothermic proton transfer to proton accepter (HCO_3, H_2O) from a proton donor ($MEAH^+$). The reactions mechanism proposed for the primary amine can be explained as follows:

Zwitterion formation for MEA:

$$MEA + CO_2 + H_2O \leftrightarrow MEAH^+COO^-(zwitterion) + H_2O \tag{2}$$

Carbamate formation from MEA zwitterion:

$$MEAH^+COO^-(zwitterion) + H_2O \leftrightarrow MEACOO^-(carbamate) + H_3O^+ \tag{3}$$

Dissociation of protonated amine:

$$MEAH^+ + H_2O \leftrightarrow MEA + H_3O^+ \tag{4}$$

Less efficiency of MEA in the stripping process shows that it has to be blended with an activator amine in order to reduce the stability of carbamate bond and minimise the energy consumption. AMP and PZ produce bicarbonate ions in an amine solution during CO_2 absorption, resulting in an easy bicarbonate breakdown and low energy requirement to release CO_2 compared to MEA.

The peak shown by the repulsive interaction was different from the attractive interaction. Repulsive interaction has only one peak and no peak is observed in the rest of the process. This is because the repulsive interaction occurs in a short time. The factor influences the repulsive interaction is the strength of N-C bond. If the stability of N-C bond is as high as carbamate ion, it requires high heat to force the repulsive interaction to happen. The intramolecular interaction (strong bonding) involves the covalent bond, metallic bond, and ionic bond. The intermolecular interaction (weak bonding) involves the van der Waals' forces, hydrogen bond, and non-covalent bond. Intramolecular interaction requires more energy for the repulsion force to happen compared to the intermolecular interaction (Kirchner and Vrabec, 2012). Figure 3 shows the repulsive interaction between the carbamate ions in the MEA solvent. The bond between –NH and C needs to be broken to allow CO_2 to react with water to form bicarbonate ion.
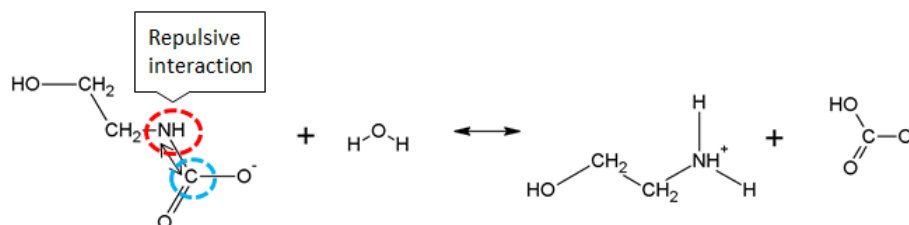

Figure 3: Mechanism for the repulsive interaction between the carbamate ions in the MEA solvent

4. Conclusions

This study elucidates the effects of different carbamate molecules with water during the regeneration process using the molecular dynamic (MD) simulation. For the stripping process, AMP and PZ carbamate amines showed stronger repulsive interactions compared to the MEA carbamate. AMP and PZ were capable to break a bond in the carbamate molecule and easily removed the CO_2 compared to the MEA carbamate. It has been shown that MEA has the limitation in the stripping process due to the lower strength of the repulsive interaction in the MEA carbamate.

Acknowledgement

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